SOLUTION KINETICS OF GYPSUM

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Abstract

Two sets of six samples of crushed gypsum and demineralized water were prepared. One set contained crystals of a grain size between 125 and 250 microns, the other set between 500 and 1000 microns. Once a week one sample from each set was dried and weighed. The ion activity product was calculated from the final weight loss of both sets, and found to be $10^{-4.46}$ for the larger-grain-sized samples at 25°C., and $10^{-4.49}$ for the smaller-grain-sized samples at 25°C. Comparison with the solubility product $10^{-4.59}$ suggests that the solutions were very near equilibrium.

During the first weeks of the experiment, the samples of smaller grains dissolved at a slightly faster rate than those of larger grains, but the difference was reduced as the solutions approached equilibrium. The rate of solution was not constant for either set of samples, probably due to the presence of very fine particles of gypsum attached to the grains during grinding, which dissolved at a faster rate due to a higher surface-area-to-mass ratio.

Introduction

A solubility experiment with powdered crystals of gypsum was performed for a period of six weeks during the autumn of 1981. The ability of gypsum to reach equilibrium with its ions in a solution of demineralized water was investigated, as well as the period of time required for this equilibrium to be reached. The rate of solution of gypsum, and the relationship of the rate of solution to the grain size of the crystals was also investigated.

These properties of gypsum are important in regard to the increasing amount of controversy over the hazards of acid rain. Acid rain, upon coming in contact with limestone, will react with the calcium carbonate as follows:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H^+ + HCO_3^-$$

A large number of buildings are constructed of limestone. The limestone on the surface of the structure is being dissolved and gypsum is crystallizing in cracks which may cause fragments of the limestone to flake off (Bloom, 1969). Gypsum also forms by the reaction of acid mine drainage water with limestone or calcium hydroxide and may be recoverable as a commercial byproduct.

Personal factors were also a consideration in my choice of this research. The gypsum was collected during July of 1981 from outcrops of shale in the Eocene Wasatch Formation

along Interstate-90 in eastern Wyoming, where it formed under similiar conditions. In addition, I am interested in the laboratory techniques of geochemistry, and enjoyed the actual experimentation involved in the research.

Experimental Methods

The crystals were crushed with a mortar and pestle and sieved to retain crystals in the -18 +35 and -60 +120 sizes, equivalent to between 500 and 1000 microns, and 125 to 250 microns, respectively. The crystals were cleaned in an ultrasonic vibrating cleaner and dried.

From each quantity of similarly-sized crystals, six portions were weighed on an analytical balance. The portions were then placed in individual beakers, and demineralized water was added to make a total volume of 300 ml. A correction was later made to increase the volume of water to 300 ml., by calculating the volume of the crystals from their weight and known density. Each beaker was covered with a Parafilm and the beakers were kept at a constant temperature of 18°C.

On the same day of the week during the following six weeks, one beaker was selected from each group. After stirring, the crystals were allowed to settle. The liquid was decanted and stored for possible later analysis, and the crystals were dried under a heat lamp. When the crystals were completely dry, they were weighed. The remaining solutions were stirred once a week.

An attempt was made to observe the solution of a large crystal of gypsum by suspending it in water, and drying and weighing it weekly. However, it was not possible to prevent large errors in the experiment due to varying water loss

from evaporation and the weekly drying of the crystal, and the results were unreliable.

Results

The net loss in milligrams was calculated from the initial and the final weights of the gypsum crystals. These results are presented in Table I. A graph of the results shows that the two sets of samples form similiar curves. Samples four and eleven did not fit the pattern of the other samples, presumably because of experimental error. Both curves level off during the fourth through sixth weeks, an indication that the solutions were approaching equilibrium. As expected, the samples of smaller grain size, and consequently of higher surface area, dissolved consistently more rapidly during the first half of the experiment than the samples of larger grain size. However, during the last weeks, the two curves tended to converge.

In order to make an accurate measurement of the solubility of gypsum it was necessary to reduce the volume of the solution by the volume of gypsum in the solutions. These were calculated from the weight and specific gravity, and were subtracted from 300 milliliters to obtain the volume of the solution. The correction was made by calculating the ratio of 300 milliliters to the actual volume of the solution, and by multiplying the weight of gypsum by this ratio. These results are presented in Table II.

The average amount of gypsum dissolved at equilibrium for each grain size was used to calculate the concentrations of Ca^{+2} and $SO_4^{=}$. The concentrations were then used to cal-

culate the ionic strength I from the equation:

$$I = \tfrac{1}{2}((\text{conc. of } Ca^{2+})\ 4 + (\text{conc. of } SO_4^{=})\ 4)$$
$$= 2\ (\text{conc. of } Ca^{2+} + \text{conc. of } SO_4^{=})$$
$$= 0.0530 \text{ moles/liter for larger grain size}$$
$$= 0.0512 \text{ moles/liter for smaller grain size}$$

These values were used to find the activity coefficients (Krauskopf, 1967). The activity coefficients were used to calculate the activities which were then combined according to the Law of Mass Action to find the ion activity product. These results are presented in Table III.

The ion activity product of a solution in equilibrium is equal to the solubility product K. K for gypsum is $10^{-4.6}$ at 25°C. (Krauskopf, 1967). The experiment was conducted at 18°C., and the discrepancy between the recorded K and the calculated values is partially corrected by the use of the Van't Hoff equation. The Van't Hoff equation is:

$$\log K_T = \log K_{To} - \frac{\Delta H_R^o}{2.303R} \left(\frac{1}{T} - \frac{1}{To} \right)$$

K_{To} is the standard value for K at 25°C., and is to be calculated. K_T is the measured value of K at 18°C. ΔH_R^o is the enthalpy change of the reaction, found by subtracting the heat of formation of the reactants from the heat of formation of the products. The values are: H_f^o $CaSO_4 \cdot 2H_2O$ = -483.06, Ca^{2+} = -129.77, $SO_4^{=}$ = -216.90, H_2O_{liquid} = -68.3174 kcal/mole (Garrels and Christ, 1965). Thus,

$$\Delta H_R^o = ((-216.90) + 2(-68.3174) + (-129.77)) - (-483.06)$$

$= -0.2448$ kcal/mole $= -244$ cal/mole

R is 1.987 cal/degree mole, T is 291.15°K., and T^o is 298.15°K. Thus, for the larger grain size:

$$-4.45 = \log K_T^o - \frac{-244 \text{ cal/mole}}{(2.303)(1.987 \text{ cal/deg mole})}\left(\frac{1}{291.15} - \frac{1}{298.15}\right)$$

$$\log K_T^o = -4.46$$

For the smaller grain size:

$$-4.48 = \log K_T^o - \frac{-244 \text{ cal/mole}}{(2.303)(1.987 \text{cal/deg mole})}\left(\frac{1}{291.15} - \frac{1}{298.15}\right)$$

$$\log K_T^o = -4.49$$

These values of K are closer to the recorded value.

The second experiment concerned the rate of solution and its relationship to the size of the gypsum grains. The grain sizes used for samples 1-6 ranged 500 to 1000 microns, with an average of 750 microns. Samples 7-12, sieved to 125 and 250 microns, had an average diameter of 187.5 microns. These average diameters were used to calculate the surface area and the weight of an average grain by multiplying its volume by the density of gypsum. These results are presented in Table IV. The weight of each sample was divided by the weight per average grain to find the number of grains per sample and from this the surface area for each sample was calculated. Next the rate of solution for each sample was calculated by dividing the millimoles of gypsum that dissolved by the time in seconds. The rate constant was then obtained by dividing the rate of solution by the total surface area. These results are presented in Table V. Finally, the rate constant was

plotted versus the time of solution. The results show that the rate of solution was higher for the grains of smaller size during the first weeks of the experiment. However, because the total surface area of the smaller-sized grains was larger than that of the larger-sized samples, the ratio of rate of solution to surface area was consistently lower for the smaller-sized samples.

The graphs of the rate constant against time for each set of samples were expected to be straight lines. Instead the graphs are parabolic curves. Holden Jr. and Berner (1979) explained this phenomenon as the result of a large number of submicron particles formed during the grinding of the crystals, which are not removed during ultrasonic cleaning. Their small size causes a large surface-area-to-mass ratio, which initially increases the rate of solution. After these fine particles have dissolved, the rate of solution becomes constant, as shown by the graph during the last two weeks of the experiment.

Summary

The objectives of this experiment were to determine whether or not gypsum would reach equilibrium with its ions in solution, and whether the rate of solution of gypsum is constant and how it depends on grain size.

After six weeks, the ion activity product was very near the solubility product of gypsum, and the solubility curves were fairly level, indicating that the solutions were very near to equilibrium.

The rate of solution was not constant, probably due to the phenomenon of submicron particles attached to the grains, but did exhibit a consistent decrease with time. The samples of the smaller grain size initially showed a more rapid rate of solution than the samples of larger grain size, but this discrepancy was reduced as the solutions approached equilibrium.

Bibliography

Blocm, Arthur L., 1969, The Surface of the Earth. Prentice-Hall, Inc., New Jersey, 152 p.

Garrels, R.M. and C.L. Christ, 1965, Solutions, Minerals and Equilibria. Harper and Row, New York, 450 p.

Holdren Jr, George R. and Robert A. Berner, 1979, "Mechanism of Feldspar Weathering--1. Experimental Studies." Geochimica Cosmochimica Acta, Vol. 3, p. 1161-1171.

Krauskopf, Konrad B., 1967, Introduction to Geochemistry. McGraw-Hill, Inc., New York, 721 p.

TABLE I

Sample Number	Initial Weight of Gypsum (grams)	Final Weight of Gypsum (grams)	Net Loss of Gypsum (grams)
1	3.6060	3.3093	0.2967
2	3.8554	3.3992	0.4562
3	3.4857	2.9157	0.5700
4	3.6680	3.1309	0.5371
5	3.5062	2.8219	0.6843
6	3.5829	2.9021	0.6808
7	1.7606	1.4470	0.3136
8	1.8960	1.4157	0.4803
9	1.9691	1.3951	0.5740
10	1.7772	1.1306	0.6466
11	1.7698	1.1401	0.6297
12	2.2648	1.5984	0.6664

TABLE II

Sample Number	Ratio of 300 ml to volume of H_2O	Recalculated Net Loss of Gypsum (grams)
1	1.0052	0.2982
2	1.0056	0.4588
3	1.0050	0.5732
4	1.0053	0.5399
5	1.0051	0.6878
6	1.0052	0.6843
7	1.0025	0.3144
8	1.0027	0.4816
9	1.0028	0.5756
10	1.0026	0.6483
11	1.0025	0.6313
12	1.0033	0.6686

TABLE III

	Samples 1-6 -18 +35 Mesh size	Samples 7-12 -60 +120 Mesh size
Average of final weight loss	0.686 grams 0.0133 moles/liter	0.663 grams 0.0128 moles/liter
I	0.0530	0.0512
Activity coefficient	0.45	0.45
Ion activity product	3.58×10^{-5} $10^{-4.45}$	3.32×10^{-5} $10^{-4.48}$

TABLE IV

	Samples 1-6 -18 +35 Mesh size	Samples 7-12 -60 +120 Mesh size
Diameter of average grain	750 microns	187.5 microns
Surface area of average grain	7.069×10^{6} square microns	4.418×10^{5} square microns
Volume of average grain	1.767×10^{9} cubic microns	2.760×10^{7} cubic microns
Weight of average grain	4.10×10^{-3} grams	6.40×10^{-5} grams

TABLE V

Sample number	Grains/ sample	Total surface area S (square microns)	Rate of solution R (millimoles per second)	R/S
1	879.6	6.218×10^{9}	9.545×10^{-6}	1.535×10^{-15}
2	940.3	6.647×10^{9}	7.344×10^{-6}	1.105×10^{-15}
3	850.2	6.010×10^{9}	6.117×10^{-6}	1.018×10^{-15}
4	894.7	6.324×10^{9}	4.321×10^{-6}	6.833×10^{-16}
5	855.2	6.046×10^{9}	4.403×10^{-6}	7.283×10^{-16}
6	873.9	6.178×10^{9}	3.651×10^{-6}	5.910×10^{-16}
7	27500	1.215×10^{10}	1.006×10^{-5}	8.280×10^{-16}
8	29610	1.308×10^{10}	7.708×10^{-6}	5.893×10^{-16}
9	30750	1.359×10^{10}	6.142×10^{-6}	4.519×10^{-16}
10	27760	1.226×10^{10}	5.188×10^{-6}	4.232×10^{-16}
11	27640	1.221×10^{10}	4.042×10^{-6}	3.310×10^{-16}
12	35370	1.563×10^{10}	3.567×10^{-6}	2.282×10^{-16}

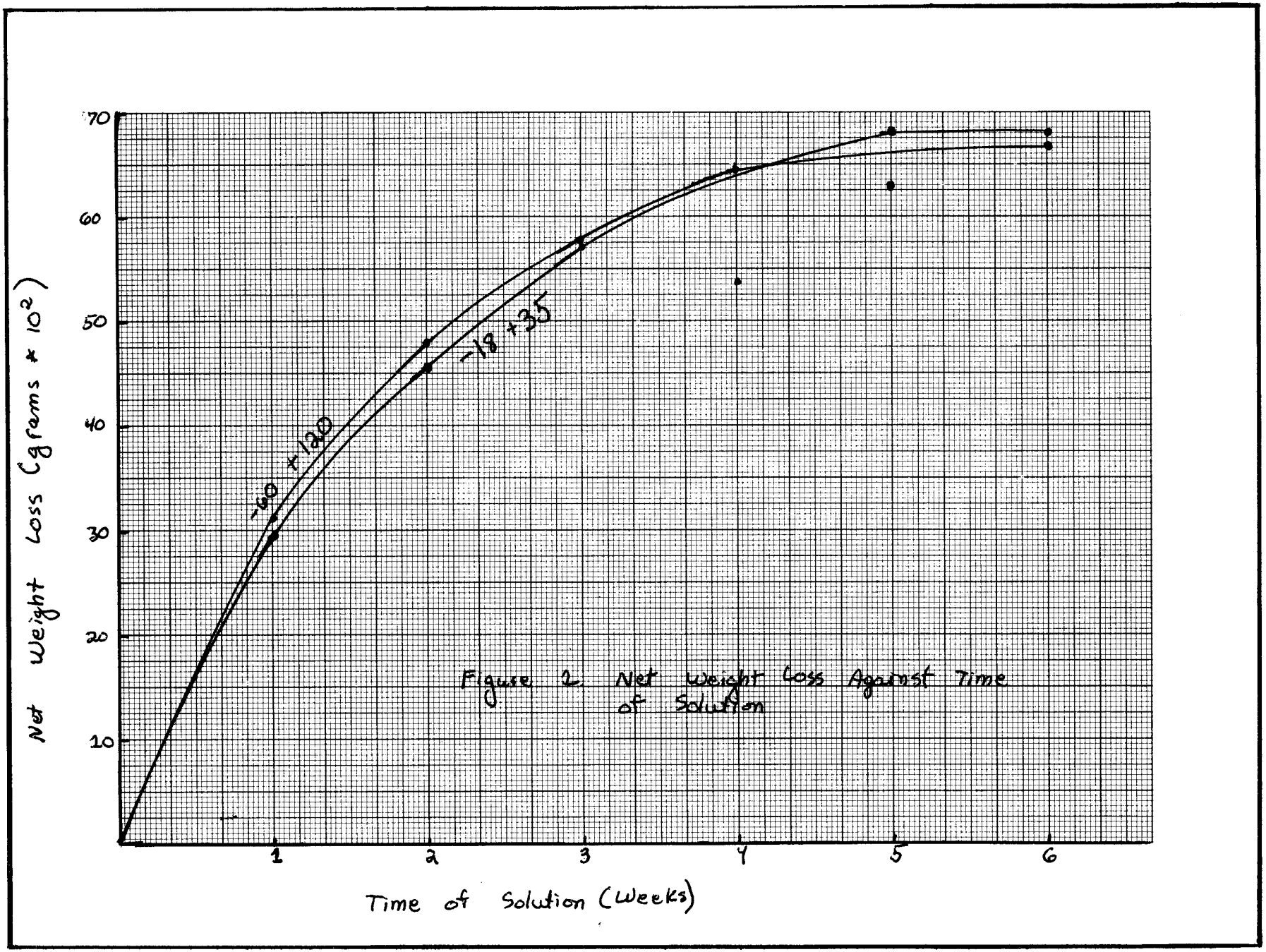

Figure 2. Net Weight Loss Against Time of Solution

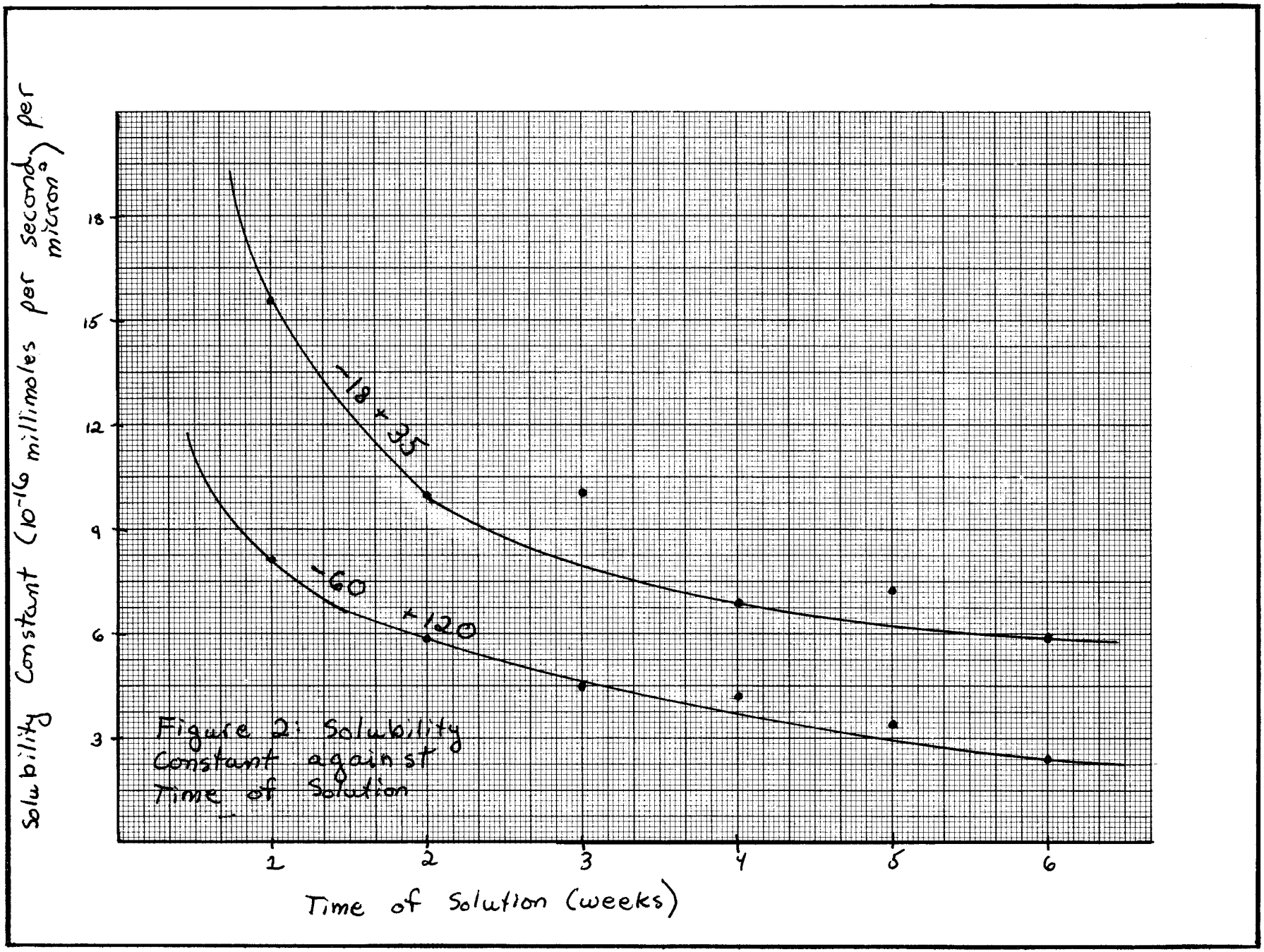

Figure 2: Solubility Constant against Time of Solution